

COMPLEX NICKEL(II) COMPOUNDS BASED ON ACYLHYDRAZONES OF AROYLTRIFLUORACETYLMETHANES

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Abstract. The article presents the results obtained from the study of nickel(II) complex compounds based on acylhydrazones of aryltrifluoroacetylmethanes.

Keywords: Aroyltrifluoroacetylmethane, acylhydrazone, IR and PMR, elemental analysis.

Introduction. In accordance with the reaction with nucleophilic reagents, aroyl trifluoroacetylmethanes can react as cis-enols or as dicarbonyl compounds, even if the concentration of the diketone form is not detectable by NMR.

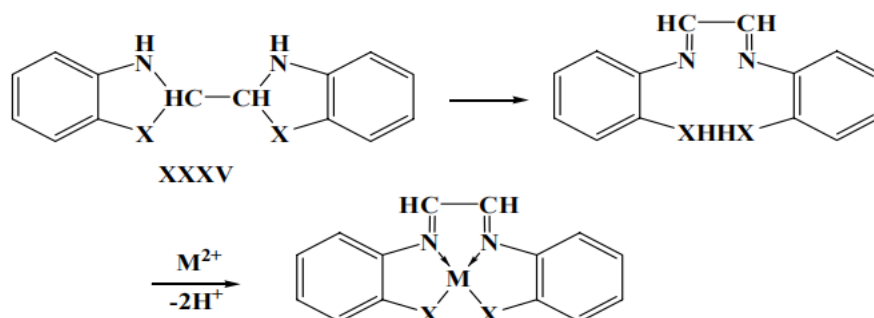
In [1,14], using a special jet NMR method, it was shown that almost completely enolized 1,3-diketones (including trifluoroacetylacetone $\text{CH}_3\text{COCH}_2\text{COCF}_3$) react with hydrazine, methyl- and phenylhydrazines in the diketone form. The low concentration of the reacting form is more than compensated by its high reactivity compared to the cis-enol form, which can be considered as a kind of vinyl analogue of the acidic structure [9]. Interaction of 1, 3-dicarbonyl compounds with acylhydrazines have not been studied in this aspect. Therefore, it is natural that it remains uncertain in what form the fluorinated 1,3diketones we have chosen will react with acylhydrazines.

However, given the above data, it seems more likely that the diketone form reacts. Based on this, we will discuss the experimental data obtained in the context of possible competition between condensation processes in the direction of trifluoroacetyl and aroyl carbonyls [14].

Literature review.

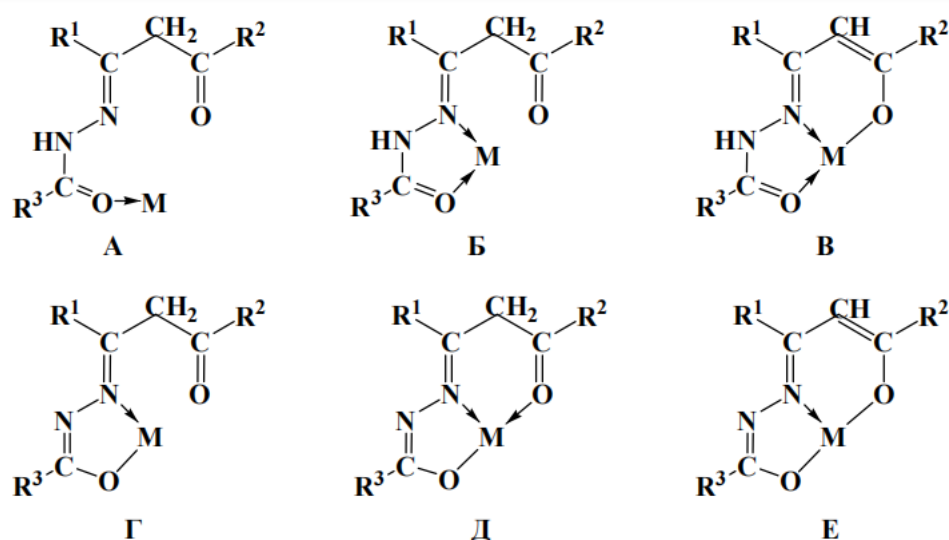
Before the work [1, 5, 6 - 14], examples of ring-chain rearrangements caused by metal ions were known in the literature only for oxazolyls and thiazolyls, five-membered N,O-, and N,S-containing heterocycles [14-15] These ligands form complexes as a result of ring opening (breaking of C–O or C–S proton bonds) and deprotonation of O–H or S–H protons. However, in all these works, only one, linear deprotonated form of the ligands, which is maximally capable of chelation, is fixed by the metalion.

In addition, what is common to all noted rearrangements is that in initial ligands, the five-membered heterocycle opens by cleavage C–O or C–S bonds:



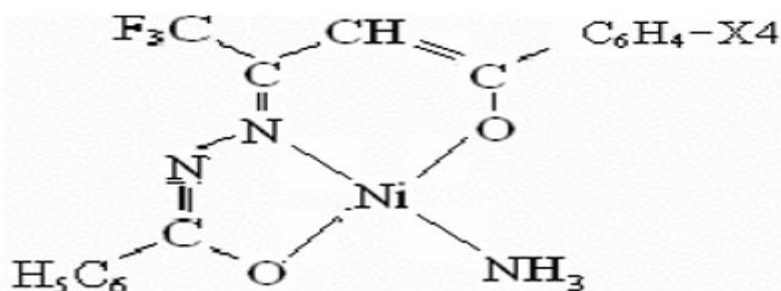
X=O;S

Ring-chain rearrangements discovered in [1, 8, 11, 15], in contrast to known cases, are characterized by much largervariety. Thus, the authors found that they tend to open the cyclenot only thiadiazoline rings, but also hydroxypyrazoline rings with cleavage connection C – N. It should be noted that the authors of these works establishedbut that depending on the metal ion, the metal: ligand ratio and the conditionvii of the complexation reaction in the case of β -dicarbonyl products compounds with acylhydrazines can be fixed by several linear ligand forms: neutral monodentate coordinated hydrazony form (A)also neutral, but bidentately coordinated engidrazine form (B) in a europium(III) complex with benzoylhydrazone benzoylacetone and complexes of nickel(II) and cobalt(II) with acylhydrazones acetoacetic ester, respectively, monodeprotonated tridentate coordination dined enhydrazine form (B)in complexes of manganese(II) and europium(III) with benzoylhydrazone of benzoyl acetone, also monodeprotonated, but bidentate - (D) or tridentate - (E) coordinated 5-hydroxypyrazoline form in complexes of nickel(II), copper(II) with aroylhydrazones of acetoacetic ester , copper(II) and cadmium(II) with 4-nitrobenzoylhydrazones of β -diketones, and finally, the doubly deprotonated tridentate coordinated form (E) in many complexes.



Research Methodology: Research methods: elemental analysis, IR, ^1H - and ^{13}C -NMR, ESR spectroscopy

Discussion of results (Analysis and results). The complex compounds $\text{NiL}^1 \cdot \text{NH}_3$ – $\text{NiL}^5 \cdot \text{NH}_3$ were obtained by the interaction of ammonia solutions of nickel (II) acetate and alcohol solutions of H_2L^1 – H_2L^5 in an equimolar ratio. Based on the results of elemental analysis, IR and PMR spectroscopy data, the complexes were assigned the following structure:



X = H ($\text{NiL}^1 \cdot \text{NH}_3$); CH_3 ($\text{NiL}^2 \cdot \text{NH}_3$); OCH_3 ($\text{NiL}^3 \cdot \text{NH}_3$); Cl ($\text{NiL}^4 \cdot \text{NH}_3$); Br ($\text{NiL}^5 \cdot \text{NH}_3$).

The IR spectra of complex compounds differ from the IR spectra of free ligands in that there are no absorption bands in the region of 1660–1700 and 3400 cm^{-1} . This indicates deprotonation of the ligands during complex formation. In many ways, the IR spectra of the obtained complex compounds are identical to the IR spectra of the studied nickel (II) complex compounds [6, 7, 9].

The IR spectra of $\text{NiL}\cdot\text{NH}_3$ complex compounds are characterized by stretching vibrations at 1595–1706 cm^{-1} ($\nu\text{C}=\text{N}$) and a single band at 1520–1530 cm^{-1} ($\nu\text{N}=\text{C}-\text{O}^-$). For example, in the IR spectrum of the complex compound $\text{NiL}^5\cdot\text{NH}_3$, the band of relatively weak intensity at 1073 cm^{-1} (Fig. 1) belongs to $\nu(\text{N}-\text{N})$, which is shifted to the high frequency region by 8-10 cm^{-1} compared to the spectrum of the free ligand [8-12].

The main vibrational frequencies ν cm^{-1} in the IR spectra of nickel (II) complex compounds

Table 1.

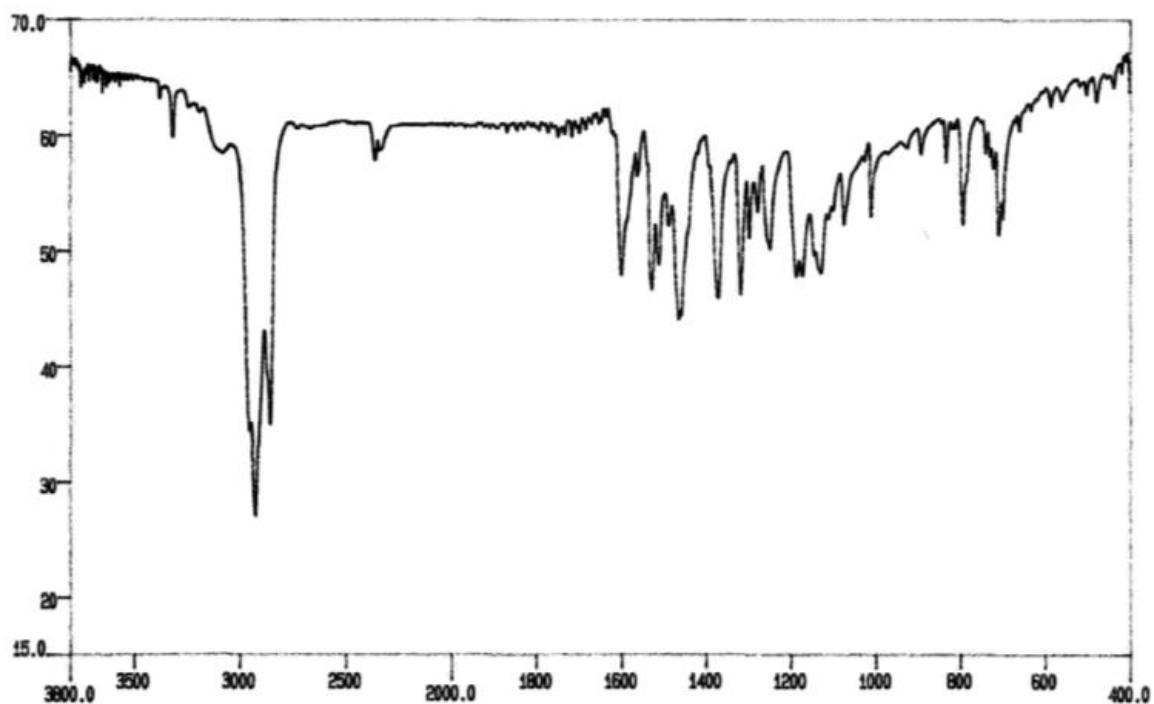
Соединение	NH_3	C–H	C=N	N=C–C=N	N=C–O ⁻	N–N	Ni–O
$\text{NiL}^{12}\cdot\text{NH}_3$	3354	2924	1569	1525	1494	1068	483
$\text{NiL}^{13}\cdot\text{NH}_3$	3344	2924	1578	1532	1507	1071	490
$\text{NiL}^{14}\cdot\text{NH}_3$	3356	2954	1600	1523	1464	1075	475
$\text{NiL}^{15}\cdot\text{NH}_3$	3344	2924	1578	1527	1488	1073	490
$\text{NiL}^{16}\cdot\text{NH}_3$	3353	2926	1587	1531	1489	1075	478
$\text{NiL}^{17}\cdot\text{NH}_3$	3354	2924	1579	1528	1484	1070	468

The isolated nickel (II) complex compounds turned out to be diamagnetic in solutions of various solvents. The results of studying the PMR spectra and diamagnetism allow us to conclude that the resulting nickel (II) complex compounds have a planar-square structure.

As an example, consider the PMR spectrum of the complex compound $\text{NiL}^3\cdot\text{NH}_3$ (Fig. 2.a). In the NMR spectrum of the $\text{NiL}^3\cdot\text{NH}_3$ complex in a $\text{DMSO}-d_6$ solution, a signal of a single vinyl proton is observed at δ 4.68 ppm. Multiplet signals centered at δ 7.37; 7.71 and 8.05 ppm are due to the protons of the aromatic nuclei of the hydrazone and β -diketone fragments of the molecule. The appearance of the signals is somewhat complicated due to their overlap. The signal from the protons of the coordinated ammonia molecule was detected at δ 1.38 ppm. and has a slightly lower integral intensity [11.14].

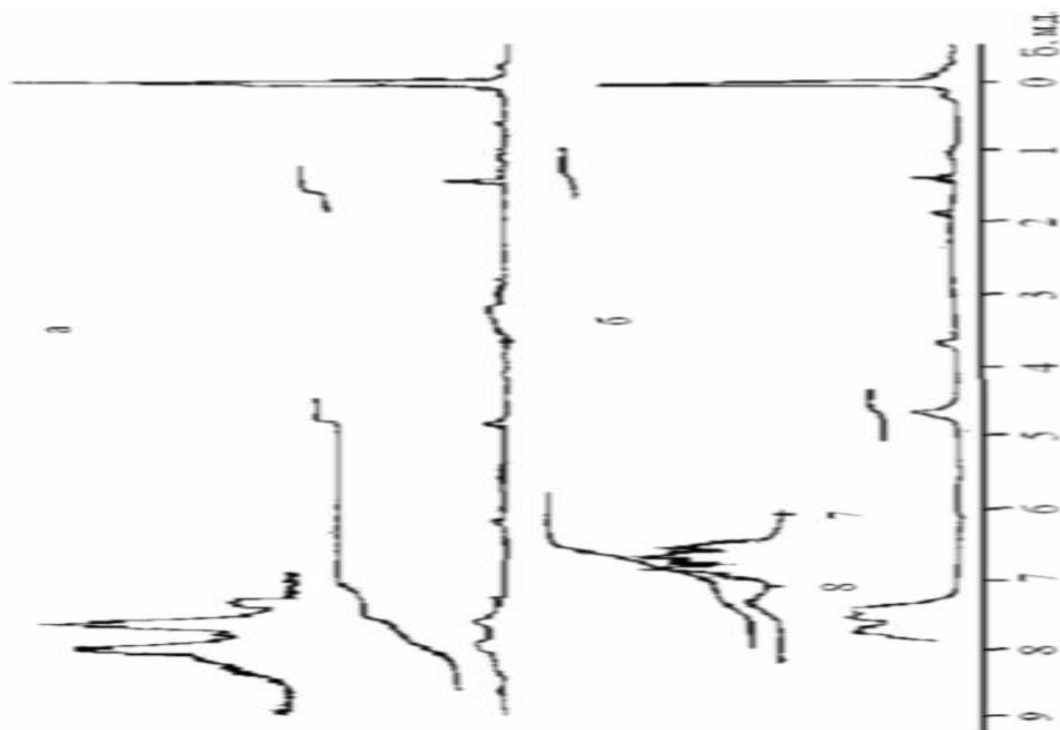
This, in our opinion, is explained by the partial replacement of the ammonia molecule with a donor solvent molecule. The NMR spectrum of the complex compound $\text{NiL}^5\cdot\text{NH}_3$ is somewhat different from the spectrum of $\text{NiL}^3\cdot\text{NH}_3$ in that in it the signals of the terminal protons are partially shifted to the downfield region.

The signal from the proton of the vinyl part of the molecule resonates at δ 4.70 ppm. Signals from protons of aromatic substituents have a more complex appearance due to the presence of bromine in the benzene ring of the β -diketone fragment of the molecule and appear at δ 7.44; 7.58; 7.75; 7.81; 8.19 ppm



Rice. 1. IR spectrum of the nickel(II) complex compound $NiL^5 \cdot NH_3$ with a structure based on 1-benzoyl-3-(4-bromophenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline (H_2L^5).

A weak signal from the protons of the coordinated ammonia molecule was detected at δ 1.36 ppm. (Fig. 2. b). The somewhat high-field shift of the signal from the vinyl proton should be explained by the formation of d- π -type dative bonds between the d-electrons of nickel(II) and the conjugate π -orbital systems of five and membered metallocycles [6,7,9,13,15].



Rice. 2. NMR spectra of complex compounds $NiL^3 \cdot NH_3$ (a) and $NiL^5 \cdot NH_3$ (b) structure in $DMSO-d_6$ solution.

Conclusion.

1. Methods of coordination of donor atoms of chelating ligands with the formation of five- and six-membered metallocycles and their structure in the crystalline state and in a solution of various solvents have been proven using IR, NMR and ESR spectroscopy methods.

2. Using NMR spectroscopy, it was established that Ni (II) complex compounds are diamagnetic and have a trans-[N₂O₂] coordination sphere.

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